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APPLICATION NUMBER: *60/415,987*
FILING DATE: *October 04, 2002*
RELATED PCT APPLICATION NUMBER: *PCT/US03/31465*

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10/4/a

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.	EL434047691US

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
J. Keith	Nelson	Niskayuna, NY

☐ Additional inventors are being named on the _____ separately numbered sheets attached hereto

TITLE OF THE INVENTION (500 characters max)

Nanometric Composites as Improved Dielectric Structures

CORRESPONDENCE ADDRESS

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☑ Firm or Individual Name — Rensselaer Polytechnic Institute

Address	Attn: Office of Technology Commercialization
Address	110 8th Street
City	Troy	State	NY	ZIP	12180
Country	USA	Telephone	(518) 276-6023	Fax	(518) 276-6380

ENCLOSED APPLICATION PARTS (check all that apply)

☑ Specification   Number of Pages   9
☐ Drawing(s)   Number of Sheets
☐ Application Data Sheet. See 37 CFR 1.76

☐ CD(s), Number
☐ Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☑ Applicant claims small entity status. See 37 CFR 1.27.
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FILING FEE AMOUNT ($)

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.
☑ No
☐ Yes, the name of the U.S Government agency and the Government contract number are _____

Respectfully submitted

SIGNATURE _____

Date   10/4/02

TYPED or PRINTED NAME   Charles F. Rancourt

REGISTRATION NO. (if appropriate)

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Docket Number: RPI-746

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Typed or printed name of person of signing Certificate

Note: Each paper must have its own certificate of mailing, or this certificate must identify each submitted paper.

Invention Disclosure Form

This form must be completed in its entirety and returned to the Office of Technology Commercialization in J-Building Room 3208 or lopezd3@rpi.edu.

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1. Title of Invention:

Nanometric Composites as Improved Dielectric Structures

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2. Inventor(s):	Position	Department/Phone
J. Keith Nelson	Professor	ECSE/6328

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3. List dates for the following:	Dates:
Invention conceived by inventor (s)	February 2001
First sketch of Invention prepared	
First written description prepared	May 2002
First model or full size device completed	
First test or operation of Invention	November 2002 (planned)
First offer of sale (Provide details in #6)	
First sale	
First public disclosure	October 2002 (planned)

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4. The Invention was made under one or more of the following circumstances

- [ ] In connection with sponsored research at Rensselaer. If so, please identify the contract and if possible, attach a copy.
- [X] In connection with any agreement of any type, which gives, any party rights whatsoever in the Invention.
- [ ] On my own time (Please provide details)

---

5. List names of each person (other than co-inventors) who have knowledge of Invention and how it was disclosed.

Professor J.C. Fothergill — University of Leicester, UK

Professor L.A. Dissardo — University of Leicester, UK

Collaborators while on sabbatical leave in the UK.

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6. List all publications, presentations or offers for sale that have been made, which include or describe this Invention.

    J.K. Nelson, J.C. Fothergill, L.A. Dissardo & W. Peasgood, "Towards an Understanding of Nanometric Dielectrics", Ann. Rep. IEEE Conf. on Elect. Insul. & Diel. Phen., 2002 (to appear) – attached.

7. List all known patents, publications and products which include or describe an Invention or technology similar to the Invention.

    A. Goel et.al., "Diamond-like Nanocomposite Coatings Possessing High Dielectric Strength", 5th Int. Conf on Cond and Break in Solid Dielectrics", IEEE, 1995, pp. 690-95.

    P.O. Henk, T.W. Kortsen & T. Kvarts, "Increasing the Electrical Discharge Endurance of DGEBA Epoxy Resin by the Dispersion of Nanoparticle Silica", High Perform Polym, 11, 1999, pp. 281-96.

8. Provide a description of the Invention along with supporting drawings, reports, photos, etc. The description should at least (1) distinguish the Invention over prior art, (2) identify the advantages of the Invention including all problems solved, and (3) list all alternative methods, materials or competing technologies which would accomplish the same results as the Invention.

Polymers of many types are commonly used as electrical insulation. In many instances, there is need to fill the polymers with materials to modify properties or to reduce the cost. In general, when this is done, the electric strength and other electrical properties are modified in a negative way.

Extensive work carried out by the inventor (using facilities at the University of Leicester, UK and partially supported by the UK EPSRC) has shown that when the filled material is dispersed in the form of nanoparticulates, the properties can be adjusted in a very positive way. It has been shown that when the filler material is reduced in physical size to dimensions of the same order as the polymer chain length, then the particles behave cooperatively with the host matrix. This is in contrast to conventional materials where the fillers have been shown to act as foreign bodies displaying interfacial properties.

In particular, the Maxwell-Wagner process associated with conventional fillers appears to be mitigated by the use of nanofillers. The attendant reduction in interfacial polarization has been demonstrated by the use of a pulsed electroacoustic technique capable of examining the charge (and hence the electric field) profile within the bulk of the insulating structure. An example is provided in Attachment 1 which shows an epoxy thermoset containing 10% inorganic oxide filler (TiO_2) with both micro and nano dimensions. It is evident that the internal fields for the new formulation are nearly a factor of 10 lower then for conventional (micro) material.

The finding is reproducible, and is mirrored in other methods of characterization undertaken:

- Thermally stimulated current analysis
- Dielectric spectroscopy
- Differential scanning calorimetry

The large changes in internal field that can be obtained strongly suggest that new nanocomposite materials can be engineered that have enhanced electric strength and improved voltage endurance properties. Preliminary dielectric strength tests undertaken in 2001 by the discloser on a LDPE /Al_2O_3 system shows this to be so. Comprehensive tests are planned for the fall of 2002 to optimize and verify this using discretionary funding in the first instance.

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9. Keywords associated with this Invention.

   dielectrics, nanotechnology, polymer composite, space charge

10. Provide a status of technology commercialization for the Invention. The description should at least
    (1) identify all possible uses for the Invention, (2) identify all companies that would be able to
    communicate the Invention, (3) best method to commercialize the Invention, and (4) indicate the status
    of work to be done prior to commercialization.

Electrical insulation is a pervasive technology which is a huge commercial business ranging from the thin films
used in the microelectronics industry to the large amounts of material used to insulate high-voltage equipment in
the power segment of the market. In most instances, the dielectric properties of the insulating structure limits the
design. A, say, 20% improvement in performance would thus have significant industrial significance and so the
substantial changes that are indicated by this disclosure are believed to be commercially important.

The availability of nanoparticles of a wide range of inorganic oxides offers the possibility of creating a range of
new materials with tailored properties and benefits eg. variation in relative permittivity and linearity.
Furthermore, it is anticipated that the use of smaller molecules as synthetic additives, chemical coupling agents,
triblock copolymers, etc. may permit an element of self assembly of these structures, and create a class of "smart"
materials based on nanocomposites to provide auto stress relief and other forms of self compensation.

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Towards an understanding of nanometric dielectrics

J. Keith Nelson[§], John C. Fothergill, L.A. Dissado and W. Peasgood
Department of Engineering, University of Leicester, UK
[§]on leave from Rensselaer Polytechnic Institute, Troy, NY, USA

Abstract: Dielectric studies are described aimed at providing an understanding of the charge storage and transport of an epoxy resin containing TiO_2 nanoparticles. Comparative results for conventionally filled composites are given, and the results discussed in terms of the underlying physics. It is shown that nanometric fillers mitigate the interfacial polarization characteristic of conventional materials with a reduction in the internal field accumulations.

Background and Vision

Nanoparticles are the fundamental building blocks in the design and creation of assembled nano-grained larger scale structures with excellent compositional and interfacial flexibility. However, rather surprisingly, the current push to develop nanomaterials based on nanotechnology has not focused much on the opportunities for dielectric materials, but rather centred on optical and mechanical applications. Nonetheless, the few examples in the literature provide encouragement that this is likely to be fertile ground. Furthermore there are good theoretical reasons why the pursuit of nanomaterials for dielectric applications may have particular promise. Some of these have been reviewed by Lewis[1] and by Frechette[2]. While the technology is in its infancy, one may speculate that it may be possible to self-assemble nanodielectrics by providing chemical structures with "hooks" which provide preferential attachment points for the nanostructured materials allowing automatic and predictable self assembly.

Fundamental Issues and Rationale

The use of conventional fillers for polymer materials is well known and is usually employed to reduce the cost of a material or to modify one of the material properties for a particular application. Examples of that would be discharge resistance, thermal expansion, etc. Often the use of such fillers will affect dielectric strength and loss in a negative way. In this context, it is thought that fundamental to controlling the dielectric strength of insulating polymers is the cohesive energy[3] density and the associated free volume[4] of a polymer structure. This may be gauged by examining the changes in electric strength (up to a factor of 10) exhibited by most polymers as they are taken through their glass transition temperature[5]. In the simplest situation, the bonding of a polymer to a filler can be expected to give a layer of "immobilized" polymer. The size of this layer is critical to the global properties (electrical, mechanical and thermal) of the composite.

Such a picture is not, however, complete since the in-filled material will give rise to space-charge accumulation and the associated Maxwell-Wagner polarization due to the implanted interfaces. Furthermore, the macroscopic theories of interfacial polarization do not incorporate a molecular approach since the response is given by relaxation equations if the wavelength is large in comparison with molecular dimensions. In considering pre-breakdown high-field conduction in pure materials, the existence of localized states within the energy band gap (close to the conduction or valence bands) is usually invoked, so giving rise to a mobility edge for electron (or hole) transport[6]. These states are essentially localized on individual molecules. This is because, unlike the strong covalent bonds of elemental crystalline solids, the intermolecular binding arises from weak van der Waals' forces that do not allow inter-molecular electronic exchange

System Characterization

In order to provide the basis for engineering nanodielectrics, this study has provided a characterization of micro- and nano-particulates of Titanium Dioxide (TiO_2) when embedded in a resin matrix. A Bisphenol-A epoxy (Vantico CY1300 + HY956) was chosen because it was benign (i.e. without other fillers or dilutents), with a low initial viscosity,

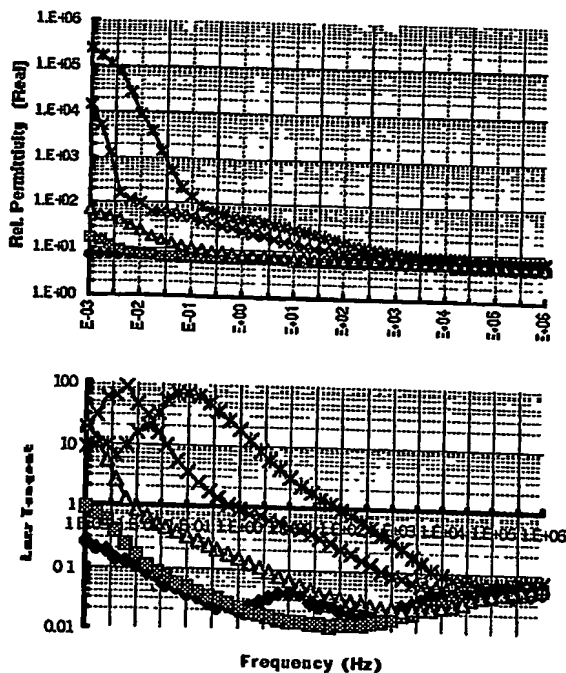| Material + Filler	Size (nm)	Loading (%)	Tg (°C)
CY1300 Resin	N/A	N/A	63.8
CY1300 + TiO_2	Micro (1500)	1	76.1
CY1300 + TiO_2	Micro (1500)	10	73.9
CY1300 + TiO_2	Micro (1500)	50	79.9
CY1300 + TiO_2	Nano (38)	1	62.9
CY1300 + TiO_2	Nano (38)	10	52.4
CY1300 + TiO_2	Nano (38)	50	62.1

Table 1 Glass transition of nano- and micro-filled TiO_2

Figure 1. Permittivity and loss tangent for micro-filled epoxy. Temps. (bottom to top) 293, 318, 343, 368, 393 K

This suggests that particles of nanometric dimensions behave in a similar way to infiltered plasticizers[8], rather than as "foreign" materials creating a macroscopic interface.

Dielectric Spectroscopy

Some insight into the way that the incorporation of materials on nanometric dimensions affect the dielectric
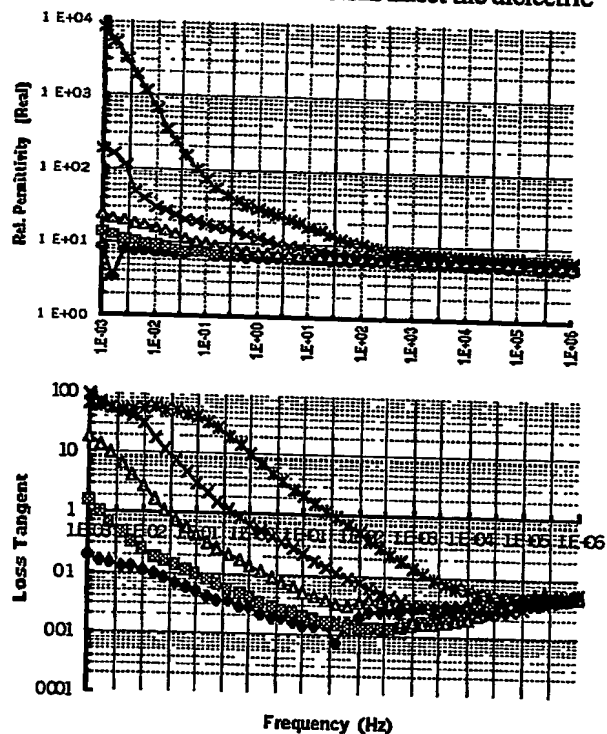

Figure 2. As Figure 1, but for nano-filled material

and with a glass transition below 100 °C. Test samples were formed by molding between polished surfaces held apart by spacers in the manner previously described[7]. The molded films ranged in thickness between 500 and 750 µm. The weighed resin and hardener were degassed at 35 °C and the relevant dried particulate fill was incorporated into the resin by mechanical stirring. Due to their small size, surface interactions for nanoparticles, such as hydrogen bonding, become magnified. This means that the particles tend to agglomerate and dispersion in resins is quite difficult, even in polymers that should be relatively compatible. Hence, in the case of nano-particles, large shear forces are needed in the mixing process to obviate unwanted clustering of the particles. For most electrical characterization, the cast film was provided with evaporated 100 nm aluminium electrodes.

Differential Scanning Calorimetry (DSC)

A Stanton Redcroft DSC 1500 calorimeter was used to thermally characterize the materials. Results on the determination of glass transition temperatures are provided in Table 1 for post-cured samples from which it is evident that the nano-material reduces T_g in contrast to the larger size particles that have the opposite effect.

properties may be obtained by examining the variation of the real and imaginary components of relative permittivity as a function of temperature and frequency. This has been done for the TiO_2 material using a Solartron H.F. frequency response analyzer (Type 1255) in combination with a Solatron Dielectric Interface, Type 1296. Examples for the micro- and nano-filled materials are shown in Figs. 1 and 2 respectively. At a nominal 10% (weight percent) particulate loading, the spectra of the resin when filled with particles of micron size (1.5 µm) are virtually indistinguishable from the base resin. This suggests that the low frequency process is probably associated with charges at the electrodes and not due to particulates in the bulk. With the filler replaced with 10% of nanometric size TiO_2 (38 nm

average diameter measured by TEM), the main differences seen relate to a marked modification of the process seen in the base resin at low frequencies and high temperatures. For the nanometric material the process exhibits a flat tan δ response at low frequencies in marked contrast to the micron-sized filler. This suggests that a percolation conduction process is operative. In the presence of the nano-filler, the mid frequency dispersion is noticeably reduced. The nano materials are clearly inhibiting motion (see PEA results below). The mid-frequency process shows a small change in estimated activation energy from 1.7 eV to 1.4 eV. The magnitude of this process is reduced in the case of nanoparticles since the side chains responsible for the mid-frequency dispersion bind to the particle surface.

Reduction of the particulate loading from 10 to 1% (by weight) did not have any very obvious fundamental changes, but the nano-filled material then does start to .exhibit a low frequency response more typical of the base resin and micro-filled material, suggesting that changes engineered by the nanomaterials do require loadings greater than a few percent.

Space charge assessment

In order to determine whether nanomaterials function cooperatively as opposed to providing sites for interfacial polarization, a Pulse ElectroAcoustic (PEA) study has also been conducted to assess the field distortions in the bulk. The method has been described elsewhere[9]. The initial distribution of stress shows
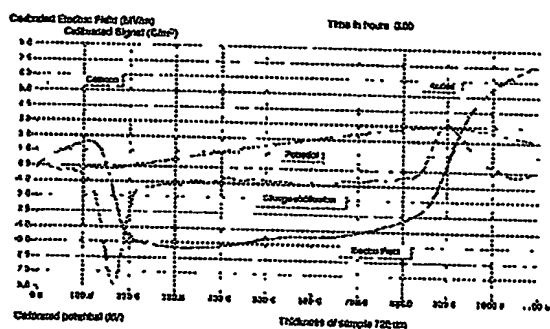

Figure 3 Initial distribution of electric field . Electroacoustic study of nano-filled material

little deviation from the nominal 4.3 kVmm⁻¹ uniform level across the bulk (see Figure 3). However, characteristic results are shown in Figs. 4 and 5 for the micro- and nano-materials (10% loading) respectively

after several hours of stressing. These plots show the charge, potential and field distributions, for a 3 kV steady DC field applied. The 1.5μm filler generates
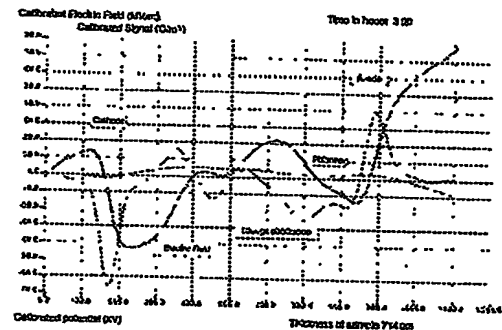

Figure 4. Pulsed electroacoustic study of micron-sized filler.

substantial internal charge, in marked contrast to the nano-material which behaves in a similar way to the
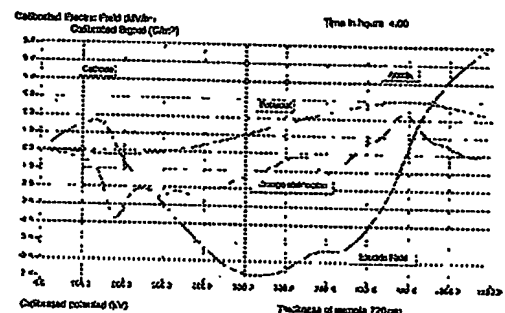

Figure 5. Pulsed electroacoustic study of nano-sized filler

base resin. Fig 4 shows several distinctive features:

(a) heterocharge accumulation of both signs leading to steep internal charge gradients
(b) a cathode field augmented to over 40 kVmm⁻¹ (10x the nominal value)
(c) field reversal yielding a point of zero stress which will greatly complicate charge transport.

Transient studies (not shown here) indicate that subsequent increase of applied voltage increases the size of the charge peaks with little change to the complex internal distribution. The stable stationary positioning of these peaks may be due the interaction of space charge with local polarization to create a self-compensating situation.

Appraisal

Very marked differences in charge accumulation are seen in filled materials depending on whether the filler has micron or nanometric dimensions. Furthermore, the characteristics suggest that, for the micron-sized filler, carriers are blocked at the anode yielding a heterocharge situation, and giving rise to the large anomalous field distortions seen in Figure 4. This behavior clearly has substantial implications for the subsequent migration of charges and probably accounts for the fact that temporal studies (not given here) show that the image charge in the cathode at first decreases and then recovers. Again in contrast to the micro-filled material, the decay of charge in the nano-filled TiO_2 is very rapid; with insignificant homocharge remaining after just 2 minutes. Although there is some injection of negative charge at the cathode, the nano-filled material is characterized by much less transport perhaps brought about by the larger density of shallower traps.

The PEA results taken in conjunction with the Dielectric Spectroscopy and DSC studies suggest that significant interfacial polarization is implied for conventional fillers which is mitigated in the case of particulates of nanometric size, where a short-range highly immobilized layer develops near the surface of the nanofiller (1-2 nm). This bound layer, however, influences a much larger region surrounding the particle in which conformational behavior and chain kinetics are significantly altered. This *interaction zone* is responsible for the material property modifications especially as the curvature of the particles approaches the chain conformation length of the polymer. Evidence suggests that the local chain conformation and configuration play major roles in determining the interactions of a polymer with nanofillers[10], as is evidenced here by the DSC results of Table 1. The polymer binding to the nanoparticles replaces some of the cross-linking and thus loosens the structure. In contrast, the micron scale case produces significant Maxwell-Wagner polarization giving rise to the characteristics of Fig.4.

In the case of nanofillers, there is evidence that a grafted layer is formed by the absorption of end-functionalised polymers onto the surface especially when the functional groups are distributed uniformly along the polymer backbone. Hence the local chain conformation is critical to determining the way in which bonding takes place (and thus the cohesive energy density). The defective nature of nanoscale particles can be expected to enhance the bonding if chemical coupling agents (CVD coatings on nanoparticles or triblock copolymers) are employed.

The large interaction zone in nanofilled polymers with reduced mobility (free volume) should be accompanied by a significant change in electrical properties. Studies of electrical behavior thus provide an opportunity both for a fundamental study of this interaction zone, and also an opportunity for optimizing performance for specific and critical applications.

The finding that conventional fillers are accompanied by substantial bulk charge accumulation is clearly a factor in the common experience of the lower electric strengths exhibited for filled materials. The mitigating effects of nanoparticles provides encouragement that nanocomposites can be engineered with strengths that are commensurate with the base polymer. Such studies are ongoing.

Acknowledgements

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[2] Frechette M.F. et al., "Introductory remarks on NanoDielectrics", Ann. Rep. Conf. On Elect. Ins. And Diel. Phen., IEEE, pp 92-99, 2001

[3] Sabuni H. and Nelson J.K., "Factors determining the electric strength of polymeric dielectrics", J. Mats Sci., Vol. 11, p1574, 1976

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SAMPLE Ti/006
10% TiO$_2$ 1.5 μm with no electrodes: 3kV for 4 Hours
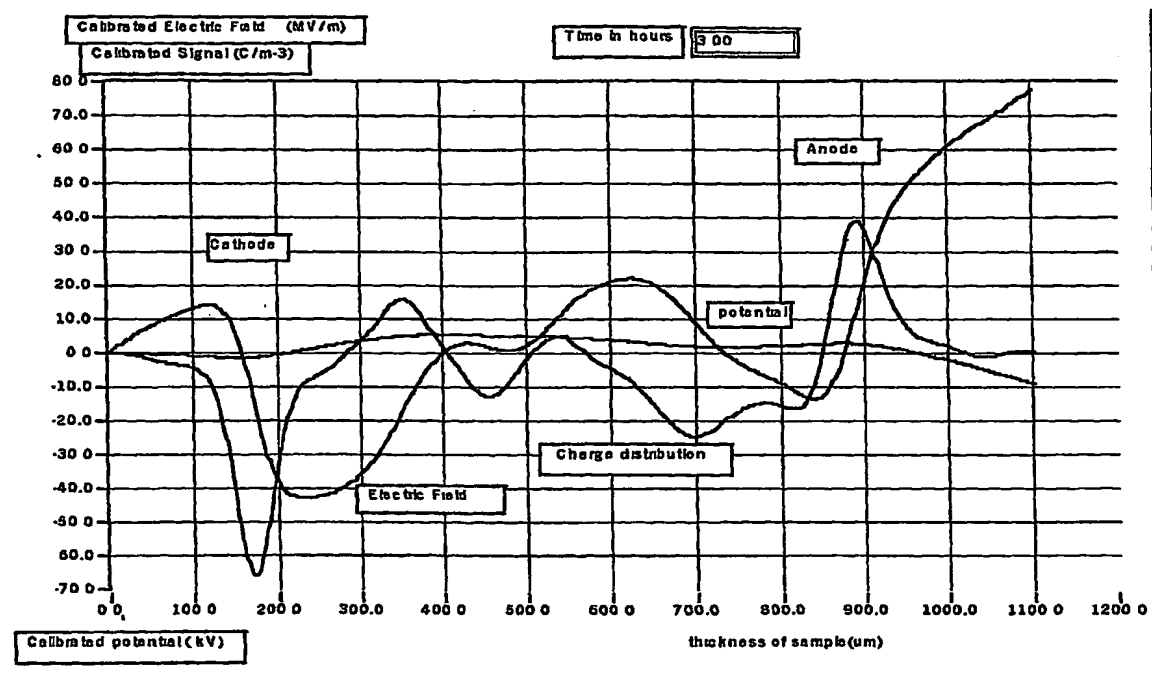
Thickness:	714 μm
Interrogating pulse	5 ns +400V, 100 pps
Scope:	5 ns, 5 mV, 1.718 μs delay
Acoustic Delay:	259 ns
Speed of sound:	2757 ms^{-1}
Sample Rate:	1.25 GSs^{-1}
Integration Range:	397 (876 thickness)
Relative permittivity:	6.0 at 100 Hz
Voltage bias:	ON 3 kV DC
Data column:	0
Filter:	6.0
Data file:	Ti006-5.txt
Timebase file:	time.txt
Reference file:	irf40new.txt (Modified PMMA reference)
Output file:	Ti006-5.doc

SAMPLE Ti/005R (REPEAT MEASUREMENT)
10% TiO$_2$ 38 nm with no electrodes: 3 kV for 4 hours
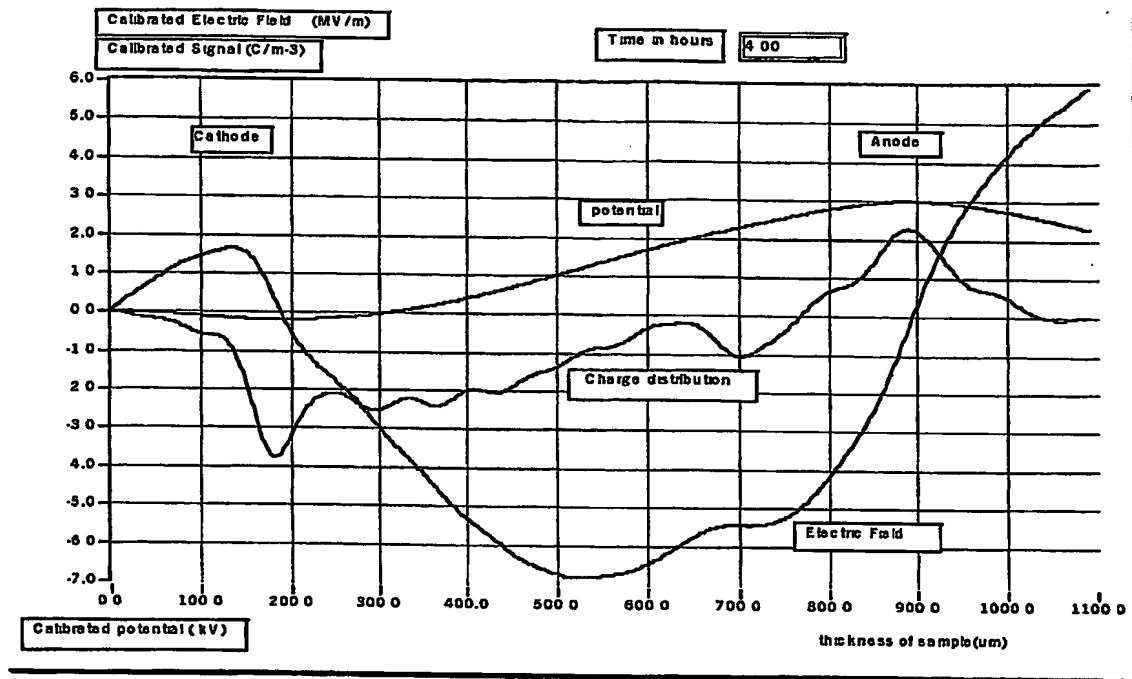
Thickness:	726 µm
Interrogating pulse	5 ns +400V
Scope:	5 ns, 5 mV, 1.724 µs delay
Acoustic Delay:	255 ns
Speed of sound:	2726 ms^{-1}
Sample Rate:	1.25 GSs^{-1}
Integration Range:	410 (894 thickness)
Relative permittivity:	6.2
Voltage bias:	ON 3 kV DC
Data column:	0
Filter:	6.0
Data file:	Ti005R-5.txt
Timebase file:	time.txt
Reference file:	irf40new.txt (Modified PMMA reference)
Output file:	Ti005R-5.doc